Modern *f*-Element Chemistry

Program Description

This project continues the unique undergraduate/graduate-level course, which is focused exclusively on the molecular chemistry of the actinide elements. The program, which is fully accredited by the University of New Mexico (UNM), features both a lecture course and selective research fellowships, and is coordinated through the Seaborg Institute for Transactinium Science (ITS). The lecture course is usually presented during the summer semester at UNM-Los Alamos (UNM-LA). The lectures provide an introduction to the chemistry of the actinide elements—an area that is frequently overlooked in most undergraduate and graduate courses. The 12-week summer research fellowships entailed participation in both the lecture course and independent research projects.

Performance Objectives and Milestones

Our aim is to continue development of an internationally recognized educational program which will (1) act as a national resource for the teaching of nuclear sciences, (2) provide a vehicle for early recruitment of the next generation of nuclear scientists and engineers, (3) offer accredited courses which can expedite a student's graduation, and (4) provide a mechanism for the career development of the Laboratory's, DOE's and National Nuclear Security Administration's staff and technicians. Due to the success from the previous years, this program was continued and grew to include new areas, e.g., general weapon technologies and dynamic experimentation. We are hopeful that this growth will continue in subsequent years, and will lead to establishment of a number of similar educational curricula in related disciplines, e.g., materials, metallurgy, and interfacial and environmental aspects of actinide science. At the conclusion of the course the students acquired a greater appreciation of the diverse role of actinide chemistry in nuclear energy and national security. With this insight, together with the introduction to the extensive research facilities available at National Laboratories, we were able to stimulate talented young researchers toward careers in actinide, nuclear, and weapons science. All previous milestones listed in our proposals, including Fellows search, presenting the course, and research presentations and publications were realized, and we are continuing this trend in the current fiscal year. In addition, we are continuing to expand and adapt the program to access larger groups of students, staff, and technicians.

Highlights of This Year's Accomplishments

We detail below our progress for the 2001 fiscal year on four separate projects: (1) the Summer lecture course at the Laboratory; (2) sponsoring of research fellows in actinide and weapons science during the summer of 2001; (3) a satellite broadcast short course, seminar and workshop series on critical skill areas; and (4) extension of the educational program to new areas of the Defense Programs mission. In support of nuclear science educational efforts, the Laboratory has established and funded this fiscal year a new position within the Seaborg Institute, Associate Director for Education. Dr. D. Webster Keogh has subsequently accepted the position. Overall, the program had 17 direct participants, including staff, technicians, and students (undergraduate and graduate) and another seven indirect participants consisting of four graduate students and three professors. These indirect contacts have resulted in an unforeseen benefit to the program. A number of fruitful collaborations

between university faculty and laboratory staff have been initiated, and further sharing of students and resources is growing.

(1) Arrangements were made to present the "Modern *f*-element Chemistry" course at the University of New Mexico's Los Alamos campus, and the course was added to the summer schedule [as course numbers CHEM 325 (undergraduate) and CHEM 537 (graduate)]. The collaboration with the broadcasting personnel at the Waste-management Education and Research Consortium (WERC) site at New Mexico State University was continued, where a rebroadcast of the signal via satellite was sent to downlink sites around the country. The class was taught from June 4th to July 27th, and we had an enrollment of 13 students, ranging from undergraduate and graduate students to technicians and technical staff.

(2) In December 2000, we distributed posters to approximately 125 chemistry departments nationwide announcing our intention to fund six Seaborg Institute Research Fellows during the summer of 2001. We also have updated and maintained our Website (http://pearl1.lanl.gov/seaborg) to provide information about the Seaborg Institute and its educational programs as well as to allow fellowship applicants to apply online. The deadline for applications was March 1st. The selected candidates were composed of two senior undergraduates (from San Jose State University and Colorado State University), and two graduate students (from the University of Texas, Austin). The majority of the Fellows were at the Laboratory for 10–12 weeks, starting in June 2001. Two of the Fellows extended their stay until October, and another two will be returning on a regular basis to perform research at the Laboratory. They attended the "Modern *f*-Element Chemistry" course in addition to performing independent research under the guidance of Laboratory scientists. During their summer research, they gave oral presentations of their work to groups of staff, postdocs and fellow students. Tours and demonstrations were also organized this year of TA-55, the plutonium processing facility, and a destruct shot (500-pound explosive test).

(3) In March 2001, we purchased satellite time for the months of June and July 2001. This purchase will provide our programs access to the same satellite 24 hours a day seven days a week during the prescribed months. This access will enhance our ability to reach other universities, DOE, and NNSA sites by simplifying the receipt of our broadcasts to a single satellite position. Within these complexes, a variety of people exist with differing educational backgrounds and needs as well as time constraints. In order to accommodate these people, we tested the use of this satellite as a potential mechanism to sponsor future short courses, workshops, and seminar series in nuclear and weapons-related sciences. The different educational approaches are designed to target the various audiences, maximizing information exchange while minimizing time requirements.

(4) In an attempt to broaden our program to include general weapons-related science we have begun to interact with other divisions in the Laboratory. On March 14, 2001, a presentation was given to the Laboratory's University Relations Committee to highlight the educational approach and successes of our program. One of the results of this briefing was an invitation to give a presentation to a group of six undergraduates visiting from UNM to discuss the Laboratory mission, the role of the Seaborg Institute, this educational program, and actinide chemistry. This visit was organized by the High Explosives Group, DX-2 and included a tour of the explosives work site. From this presentation, an invitation was extended to present similar information to all student mentors in the Dynamic Experimentation (DX) Division on April 4 and 10, 2001. During these meetings, formal inclusion of a number of DX students into this program was made.

In order to continually improve the quality of the program, feedback from both UNM course surveys and custom-made course evaluations is being employed. These surveys seek input on the specific course topics, potential interest in additional classes in future years, the attitudes of the students toward actinide chemistry and the possibility of future career plans within actinide or nuclear science. In addition, we compiled a complete listing of e-mail addresses of all students participating in the courses, in order to track the future educational or employment endeavors of the students. This has enabled us to judge the potency this program has in stimulating interest among young scientists in the "Nuclear Future." This fiscal year we have begun to see the effect this educational program is having. We had four research fellows during our first year, FY99, two undergraduates and two graduate students. All four of these students have pursued careers in the nuclear science arenas. The two graduate students will be returning to the Laboratory as postdoctoral research associates, one of the undergraduate students is now at Stanford University in a Ph.D. program studying the behavior of uranium in the environment, and the other undergraduate has entered the Navy as a Nuclear Propulsion Officer. From the group of this year's Fellows, one of the undergraduate students has hired on as a full-time graduate research assistant, two of the graduate students will be returning to the Laboratory on a regular basis, and one undergraduate and one graduate will be returning next year to continue their independent research. We are extremely encouraged by these positive results, especially since all of the students have indicated that the experience with this program has guided their current pursuits in nuclear science.

The Research Fellows from the summer of 2001 all had an extremely productive time at the Laboratory, and a number of manuscripts have been published in this fiscal year:

(1) The Expanded Porphyrin Hexaphyrin(1.0.1.0.0.0): A Novel Ligand for the Complexation of Actinide Cations Uranyl (UO_2^{+2}) and Neptunyl (NpO_2^{+}); Jonathan L. Sessler, Daniel Seidel, Anne E. Vivian, Vincent Lynch, Brian L. Scott, and D. Webster Keogh, *Angew. Chemie. Int Ed. Eng.* 2001, *40*, 591-594.

(2) Synthesis and Structural Characterization of the Lanthanide Schiff-Base Complex, Michael Essig, D. Webster Keogh, Brian L. Scott, John G. Watkin, *Polyhedron* 2001, *20*, 373-377.

(3) A Model for Trivalent Actinides in High Carbonate-Containing Media: Structural Characterization of the Lanthanide Tetracarbonate $[Co(NH_3)_6][Na(\mu\text{-}H_2O)(H_2O)_4]_2[Ho(CO_3)_4] \cdot 4H_2O$; Deborah L. Bond, David L. Clark, Robert J. Donohoe, John C. Gordon, Pamela L. Gordon, D. Webster Keogh, Brian L. Scott, C. Drew Tait, and John G. Watkin, *European Journal of Inorganic Chemistry* 2001, 2921-2926.

(4) A Mechanistic Study of the Samarium(II) Mediated Reduction of Aryl Nitro Compounds to the Corresponding Aryl Amines. The Crystal Structures of $\{Sm[N(SiMe_3)_2]_2(thf)\}_2(\mu^2\text{-}O)$ and $[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh)Sm[N(SiMe_3)_2]$; Erik D. Brady, David L. Clark, D. Webster Keogh, Brian L. Scott, John G. Watkin, *J. Am. Chem. Soc. Accepted.*

The Nuclear Weapons Mission of both Defense Programs and the Laboratory is to ensure confidence in the safety, reliability and performance of US nuclear weapons without nuclear testing. In the absence of nuclear testing, this requires a science-based approach to stockpile stewardship. Decisions must be made based on sound technical understanding and expert judgment developed through theory, experiment, and simulation. Therefore, one of the principal long-term issues facing the DP Laboratories is that of maintaining the quality of our scientific staff. Of grave concern is that a large fraction of Laboratory staff could retire within the next decade (42% of Laboratory technical staff are aged 50 or older), and their expertise and knowledge must be transferred to a new generation. From this

perspective, "Modern *f*-Element Chemistry" is one of the crucial components of the science and technology needed to reconstitute an underground nuclear testing or nuclear weapons production capability. It is sobering to recognize that virtually all of the Laboratory new hires over the past 20 years lack formal training in either this discipline or nuclear and radiochemistry. Our educational program is designed to provide overlap to transfer this corporate knowledge to current laboratory and DOE staff and to build a scientific base for future programmatic success. On page 29 of the Chiles Commission Report "Maintaining United States Nuclear Weapons Expertise," it is stated that "Post-doctoral, intern, and continuing education programs should be emphasized as especially important recruitment tools, and special emphasis should be placed on making the nuclear weapons complex an attractive place for women to work, given the increasing fraction of women in the scientific and engineering programs at American universities." A combined total of 91 students have registered for our workshops and summer course. In addition to the students enrolled at UNM-LA, local Albuquerque and distance-education sites coordinated through either the UNM or WERC systems led to the registration of students from UNM's Albuquerque campus, New Mexico Tech in Socorro, and Carlsbad Field Office. This course attracts a diverse audience representing a number of ethnic and minority groups. Over the three-year duration of this program, 40 of our students and Fellows have been women, representing 44% of our total enrollment. We are extremely pleased with the relatively high proportion of female students, technicians and postdocs who have signed up to take the *f*-element course, and we will strive to maintain this level of interest.

The six Research Fellows, who joined the Laboratory this year, were:

Cynthia Bolme – Junior at University of California, San Diego. Cyndi worked within the High Explosives Science and Technology group (DX-2). Cyndi's mentor for the summer was Dr. Steve Son. Their work focused on measuring the pressure dependence on the deflagration rates of high explosives. The secondary goal of the research was to investigate how cracks and other damage in explosives impact the deflagration.

Leilani Conradson – Senior at San Jose State University. Leilani took residence in the Nuclear Materials and Technology Division office. Her main responsibilities were the organization for scientific experiments at Stanford Synchrotron Source and program development for the Nanoscale Technology Conference. Leilani's summer mentor was Dr. David L. Clark.

Danielle Garcia – Graduate student at the University of New Mexico. Danielle is studying for a doctorate degree in pharmacy. Her interest in the fellowship program stemmed from the ability to work with analytical techniques for organic compounds. Danielle was mentored by Dr. Mary Campbell from the High Explosives Science and Technology group (DX-2). The exact work involved thermal analysis of explosives and their binders by dynamic mechanical analysis. The data they collected over the summer were used to support stockpile surveillance in analyzing whether lifetimes for the safe handling and reliable performance of the Stockpile can be determined and extended.

Anne E. Gorden – Graduate student from the University of Texas. Annie is in the doctoral program at the University of Texas in the Organic Chemistry department. Her mentor this summer was Dr. D. Webster Keogh from the Chemistry and Nuclear Materials Technology Divisions. Annie resided in the Structural Inorganic Chemistry (C-SIC) Group during the summer and will come back to the Laboratory in the spring of next year. Her research project for this summer consisted of synthesizing novel ligands for binding light actinide elements, uranium, neptunium and plutonium. The ligand systems she has been working with are expanded porphyrins. Annie has been able to show that by

varying the size of the cavity selectivity over not only the metal center but also the oxidation state. Her work has both applied and fundamental implications. Figure 16 shows UV-Vis-NIR spectra of the free ligand isoamethyrin and once it is bound to Np(V). A crystal structure of the metal complex is also shown. These expanded porphyrin ligands are intensely colored with molar extinction coefficients in the hundreds of thousands and dramatic changes in the color occur when a metal is complexed. As a result colorimetric indicator systems could eventually be developed around this technology to detect actinide contamination down to 0.1 mM.

Piyush Shukla – Graduate student from the University of Texas. Dr. John Gordon from the Chemistry Division mentored Piyush this past summer. As a result of Piyush's hard work and enthusiasm, a permanent collaboration between Dr. Gordon and Prof. Alan Cowley, Piyush's graduate advisor, has been established. Piyush worked in the area of main group chemistry, developing concepts and new ligand systems, which will be applicable to lanthanide and actinide chemistry.

Recently there has been a great deal of interest in using (aromatic) diimine ligands to support complexes capable of promoting new C-H activation and olefin polymerization chemistries. Traditionally, aromatic diimines are generated via the reaction between an aniline and a diketone (in the presence of a dehydrating agent). We are particularly interested in accessing diimine ligands that contain perfluorinated aromatic groups, since these should confer a high degree of electrophilicity at the metal centers we choose to study. This general class of ligand appears to largely inaccessible by traditional methods (due to the lack of nucleophilic character of the anilines). As an alternative synthetic approach, Piyush investigated the chemistry of aluminum complexes containing anilido fragments and their application in the synthesis of new diimines. Not only did he prepare and characterize several new organometallics, but he also demonstrated the potential utility of the

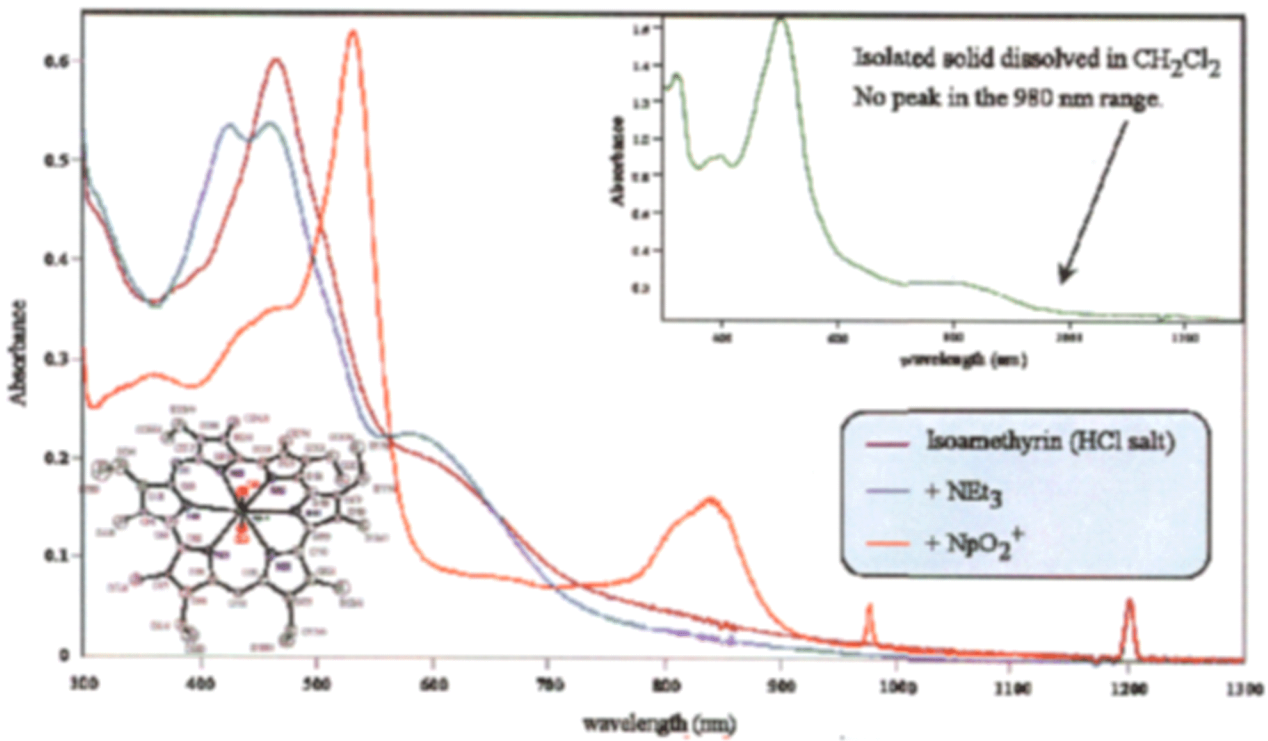

Figure 16. UV-Vis-NIR spectra of the free ligand isoamethyrin.

method in the synthesis of a number of new a-diimine, b-diimine and b-ketimine ligands that we plan to use in the synthesis of new complexes of the p, d and f-block elements.

Bridget Williams – Undergraduate student from Colorado State University. Bridget joined Los Alamos National Laboratory as a student scientist to pursue fundamental research of the lanthanide and actinide elements. Bridget is motivated to become a leader in this field and has chosen to continue her research at Los Alamos for the remainder of the 2001/02 academic year. She will begin her graduate research and education in chemistry at the University of Wisconsin beginning in the fall of 2002. Bridget has been mentored in her work by Dr. Warren J. Oldham, a staff scientist in the Nuclear Materials Technology Division. Bridget's work is motivated by a desire to develop sustainable and nonpolluting chemical technology for actinide recovery and purification. In this effort Bridget has explored the behavior of metal complexes in novel, environmentally benign solvents called room-temperature ionic liquids. Room-temperature ionic liquids are low-melting (below room temperature) organic salts composed of organic cations and weakly coordinating anions. The perception of ionic liquids as "green" solvents is based principally on their nonvolatility and significantly reduced flammability hazard compared to more familiar organic solvents (Fig. 17). Ionic liquids may also promote interesting and distinctly different reaction chemistry promoted by a novel and easily manipulated chemical environment. Ionic liquids are capable of solvating and stabilizing highly charged metal species, while maintaining good solubility of nonpolar organic materials. The distinctive ionic character of these solvents also provides highly electrically conductive media that can be exploited in electrochemical applications. Bridget is working to characterize the basic coordination chemistry and electrochemical behavior of lanthanide and actinide complexes in the ionic liquid medium. Her work will form the scientific basis of advanced, next generation, sustainable nuclear technology.

Future Plans

Technician and Student Development

We will be distributing an announcement for the future courses and workshops to students, postdocs and technicians who work within the Chemistry, Nuclear Materials Technology,

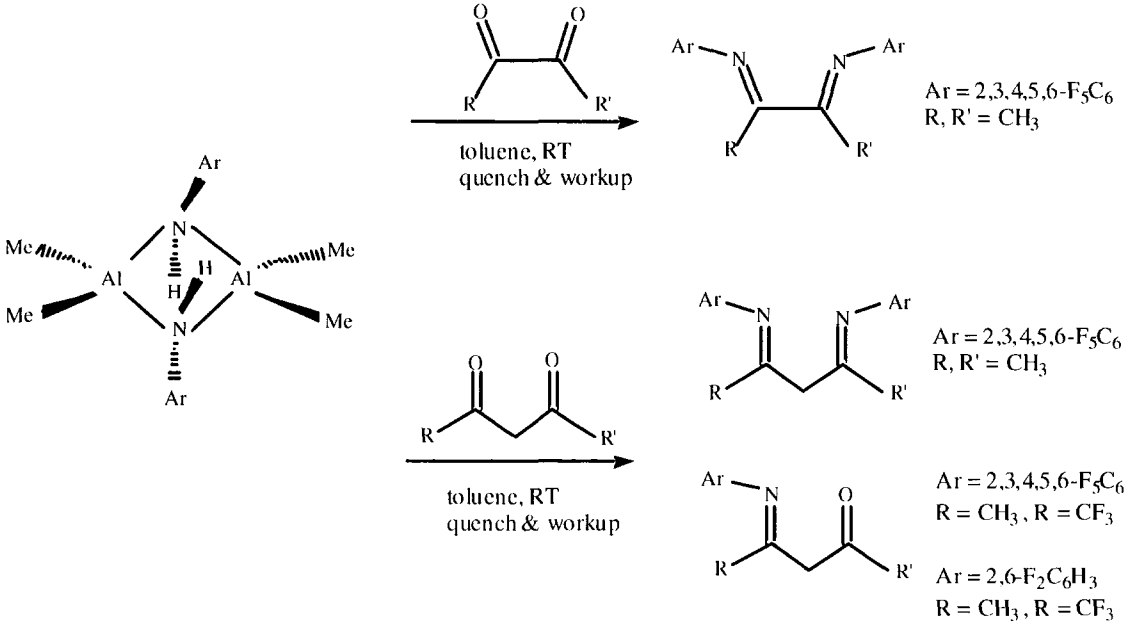

Figure 17. Ionic character of "green" solvents.

Materials Science Technology, and Explosives Divisions at the Laboratory. The announcements will be posted on both the Laboratory's student and postdoc Web pages so that they will be available to all incoming students. We have previously had extremely positive responses to the course announcement from many Laboratory employees, and a significant number have registered to take the course.

Short Course, Workshop, and Seminar Series
As mentioned above, satellite broadcast testing for short courses, workshops and seminar series was performed during the months of June and July 2001. Future programs will be run as frequently as possible with a target of at least one per month. The current topics under consideration for these presentations are Plutonium Metallurgy, Spectroscopic Techniques in Actinide Chemistry, and Separations Science.

Summary

We have described the activities, which have taken place in FY01 for this program as well as comprehensive data encompassing the first three years. Our intention is to expand the scope of the program to the point at which students will be able to take fully-accredited courses not only in *f*-element chemistry, but also in closely allied subjects such as plutonium metallurgy, environmental actinide chemistry, physical methods and interfacial actinide science.

Institutions represented by students participating in Nuclear Science Education for the 21st Century: Modern *f*-Element Chemistry.

University of New Mexico
New Mexico State University
University of California, San Diego
San Jose State University
University of Texas
Colorado State University